The Effect of Nonspherical Shape of Liquid Phase Embryos on the Rate of Homogeneous Nucleation

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Abstract—Stationary nucleation in supersaturated vapor is treated for the case in which the equilibrium shape of liquid phase cluster embryos is other than spherical. An expression is derived for the chemical potential of a cluster of spheroidal shape, whence it follows that the cluster surface energy increases upon the increase in its deformation faster than its surface area. The virtual chain model is proposed for the purpose of interpretation of the size dependence of the chemical potential. The calculated values of the nucleation rate in cesium vapor prove to be less than follows from the classical theory, which is in qualitative agreement with experiment.

1. INTRODUCTION

The main assumption of the classical nucleation theory [1, 2] is the liquid drop model, in which the properties of a cluster containing several tens of molecules are described by quantities characteristic of a macroscopic droplet (density, surface tension, saturation pressure). Up to now, efforts of numerous researchers were mainly aimed at the improvement of this classical model, which implies its thermodynamically consistent formulation, inclusion of additional correction factors, etc. (cf., [3, 4]). Difficulties of the classical theory and its modern formulations are associated with poor adaptability of the macroscopic approach to the description of a microscopic cluster and manifest themselves as discrepancies (sometimes fairly significant) between nucleation rates calculated theoretically and observed experimentally.

An alternative way of describing small clusters containing the number of molecules not greater than the coordination number in phase was proposed in the model of [5, 6], which involves only the microscopic parameters characterizing the intermolecular potential instead of macroscopic parameters. In the case of an arbitrary number of molecules contained in the cluster, its chemical potential is written as a linear function of numbers of molecules at the cluster surface and inside the cluster. Nucleation rates calculated by above-mentioned model describe correctly the experimentally observed deviations from the classical theory toward both the increase and decrease of the nucleation rates for water and mercury.

Within the framework of this model, the numbers of surface and inner molecules are estimated, assuming that the cluster is, on the average, spherically symmetric and that it is a nucleus surrounded by the surface layer. However, this assumption may prove invalid in some cases. In fact, numerous data indicate that the equilibrium shape of alkali metal clusters with open electron shells differs from the spherical one [7–9]. It is clear that the nucleus must vanish in the limit of strong deformation of the cluster; i.e., all molecules prove to be surface ones. This causes a much greater increase in the cluster surface energy than in the case of including only the increase of its surface area. This fact results in an increase of effective surface tension of the cluster and drop of the nucleation rate as compared to the classical theory [2].

In this paper, the results of [5, 6] are generalized to the case of nonspherical cluster shape. In Section 2, equilibrium vapor containing nonspherical clusters is treated; in Section 3, homogeneous nucleation is treated in a vapor containing such clusters; statistical interpretation of the expression for the cluster chemical potential, which forms the basis of the model, is given in Section 4; the results are analyzed in Section 5.

2. SPHEROIDAL CLUSTER MODEL

Consider first the case of thermodynamic equilibrium. The system under study is a mixture of ideal gases, the monomer molecules and clusters. We assume that the chemical potential of a cluster is a linear function of the numbers of surface \( q_0 \) and inner \( q_1 \) molecules (the latter form the cluster nucleus; for these molecules, the coordination number \( N \) is equal to this quantity in liquid). Then, the equilibrium number density of clusters containing \( g = q_0 + q_1 \) molecules is defined by formula [5]

\[
\bar{n}_g = n_1 \exp[(g - 1) \ln S - (q_0 - 1) \ln (K_2/n_1)],
\]

where \( n_1 \) is the monomer number density; \( S = n_1/n_{1s} \) is supersaturation; \( K_2 = n_1^2/\bar{n}_2 \) is the dimer equilibrium constant; and the value of the parameter with the subscript \( s \) is taken at saturation line. In deriving the size distribution (1), no assumptions were made concerning
the shape of a cluster, which defines the ratio of the numbers \( q_0 \) and \( q_1 \).

In order to estimate the numbers of surface and inner molecules for a cluster with nonspherical shape, we will generalize the spherical cluster model to this case. The easiest way to do this is to introduce the local formulations of assumptions of the above-mentioned model. According to [5, 6], the inner molecules are present in a cluster only at \( g > N \) (at \( g = N + 1 \), the cluster nucleus contains a single molecule and has the size of \( r_c = (3/4\pi n_i)^{1/3} \), where \( n_i \) is the molecule number density in the liquid phase); the difference between the radii of a cluster and its nucleus is independent of \( g \) and defined by the properties of a concrete substance and temperature. The first condition is a straightforward consequence of the definition of the numbers of surface and inner molecules. These conditions may be formulated in another form applicable to nonspherical clusters: the minimum curvature radius of the surface of cluster nucleus is equal to \( r_c \); the distance between the surfaces of a cluster and its nucleus is independent of \( g \) and cluster deformation and constant at all points of the surface of cluster, with one possible exception for those points in which the curvature radius is equal to \( r_c \). The restriction of curvature radius is due to the fact that each inner molecule must have \( N \) nearest neighbors. As the deformation of a cluster increases, the nucleus decreases in size. Obviously, the minimum nucleus, as in the case of a spherical cluster, has the shape of a sphere of radius \( r_c \). In the limit of extremely strong deformation (oblate or prolate cluster), all molecules become surface ones irrespective of their number, because none of the molecules has \( N \) nearest neighbors.

We will restrict ourselves to the case of axial symmetry of clusters. The deformation of a degenerate ellipsoid with semiaxes \( R_x \) and \( R_y = R_z \) (of a spheroid) is characterized by a single parameter \( \beta = 2(R_y - R_z)/(R_y + R_z) \). One can approximate with adequate accuracy the shape of a nucleus of a fairly large cluster by a spheroid with semiaxes \( R'_y = R_y - \lambda r_c \) and \( R'_z = R_z - \lambda r_c \), where \( \lambda r_c \) is the surface layer thickness. For a small cluster, it is necessary to additionally restrict the minimum curvature radius of the nucleus \( \kappa = \min \{ (R'_y)^2 / R'_y, (R'_z)^2 / R'_z \} \) by the quantity \( r_c \). Then,

\[
\frac{R'_y}{r_c} = \min \{ (\rho_x - \lambda, (\rho_x - \lambda)^2 \}
\]
\[
\frac{R'_z}{r_c} = \min \{ (\rho_x - \lambda, (\rho_x - \lambda)^2 \}
\]

at \( \kappa \geq r_c \), where \( \rho_{x,z} = R_{x,z} / r_c \); at \( \kappa < r_c \), the nucleus is absent \( (q_0 = g) \).

At \( \kappa > r_c \) (large clusters), the volume of a nucleus is equal to \( V_1 = \frac{4\pi}{3} r_c^3 (\rho_x - \lambda)^2 (\alpha \rho_x - \lambda) \), where \( \alpha = (2 + \beta) / (2 - \beta) \), and that of the surface layer, \( V_0 = \frac{4\pi}{3} r_c^3 \{ \alpha \rho_x^3 - (\rho_x - \lambda)^2 (\alpha \rho_x - \lambda) \}. \)

We will designate the concentration of molecules in the surface layer by \( \eta n_i \) (it is assumed that in the nucleus it coincides with \( n_i \)). Then, the total number of molecules in a cluster may be written in the form

\[
q = (1 - \eta) (\rho_x - \lambda)^2 (\alpha \rho_x - \lambda) + \eta \alpha \rho_x^3.
\]

The solution of this transcendental equation with respect to \( \rho_x \) defines the quantity \( q_0 = \eta n_i V_0 / \rho_x \). At \( \alpha = 1 \) (spherical cluster), equation (3) reduces to that obtained in [5, 6],

\[
q = q_1 + 3\omega q_1^{2/3} + 3\omega \lambda q_1^{2/3} + \omega \lambda^2,
\]

where \( \omega = \lambda \eta = (4\pi/3) \sigma_0 r_c^2 / k_B T \ln(K_2 / n_i) \); \( k_B \) is the Boltzmann constant; and \( \lambda = \sqrt{N/\omega - 3/4} - 3/2 \).

For small clusters, \( (\kappa = r_c) \), one should distinguish between the cases of oblate \((\beta < 0)\) and prolate \((\beta > 0)\) clusters. In the former case, \( R'_y = (R'_y)^2 / R'_c \) and \( R'_z = r_c q_1^{1/5} = R_y - \lambda r_c \), and the number \( q_1 \) is the solution of the equation

\[
g = (1 - \eta) q_1 + \eta \alpha^2 (q_1^{1/5} + \lambda)^3.
\]

In the latter case, \( R'_y = (R'_y)^2 / r'_c \) and \( R'_z = r_c q_1^{1/4} = R_z - \lambda r_c \), and we have

\[
g = (1 - \eta) q_1 + \eta \alpha (q_1^{1/4} + \lambda)^3
\]

instead of (5).

Equations (1), (3), (5), and (6) define the equilibrium number density of clusters provided the size dependence of the deformation parameter \( \beta(g) \) is known. It follows from these equations that \( q_0 \) is always greater at \( \beta \neq 0 \) than at \( \beta = 0 \). Therefore, the effective surface energy of a cluster is also greater.

An example of nonspherical clusters is provided by the alkali metal clusters. Their only valence electron becomes collective easily; therefore, the electrons fill the shells in the self-consistent field of the entire cluster. In so doing, the spherical symmetry is broken if the total angular momentum of a system is other than zero, and deformed states prove to be advantageous in energy. Sodium clusters provide the traditional object of research (see review [9]). Calculations performed by quantum chemistry methods, as well as within the framework of the self-consistent spheroidal jelly model and ellipsoidal shell model, support this conclusion qualitatively. They are also in good quantitative agreement. In fact, the values of axially symmetric deformations of sodium clusters calculated in [7] and [8] differ by no more than 20–30%. The largest clusters containing more than a hundred molecules were treated for the shell model [7]. A characteristic feature of these results is the emergence of "magic" numbers \( g = 8, 20, 40, \ldots \), corresponding to closed electron shells or spherical
cluster configurations. The equilibrium deformations calculated in [7] correspond to \( T = 0 \); however, their variation at nonzero temperature will change little provided the following condition is valid:

\[
E(0) - E(\beta) \gg k_B T,
\]

where \( E \) is the energy of a deformed cluster per atom, and the value of \( \beta \) corresponds to its minimum.

3. NUCLEATION IN CESIUM VAPOR

Consider homogeneous nucleation in supersaturated cesium vapor, while bearing in mind comparison with experiment [10]. Unfortunately, no data are available in the literature on deformation of cesium clusters: calculations, which were few in number, were performed within the framework of spherically symmetric models at \( T = 0 \). However, one can use the principle of similarity of properties, which holds for all alkali metals except for lithium [11], and assume that the order of filling the electron shells is the same for clusters of all alkali metals, and, therefore, the values of deformation \( \beta \) do not differ much for cesium and sodium. Such an approach is justified if there is no sharp dependence of the sought quantities on this parameter. Indeed, the calculated nucleation rate proves to be independent of the deformation parameter during its variation within 20–30% (which corresponds to the accuracy of calculation of \( \beta \) in [7]). Thus, the theory based on the use of values of \( \beta \) calculated for sodium clusters at \( T = 0 \) for description of cesium clusters at finite temperatures may claim to be at least a qualitative illustration of possible effects.

Figure 1 shows the minimum work of cesium cluster formation in supersaturated vapor \( \Delta \Phi_g = k_B T \ln(n_g/\bar{n}_g) \), calculated by formula (1), where the values of \( q_0 \) were found by solving equations (3), (5), and (6). The density, surface tension, pressure of saturated cesium vapor, and value of the dimer equilibrium constant are borrowed from the reference book [11]; \( N = 8 \). The values of the deformation parameter of sodium clusters \( \beta \) for \( g \leq 40 \) are borrowed from [7]. According to these data, the values of \( \beta \) at \( g > 34 \) decrease noticeably as \( g \) increases; for \( g > 40 \), systematic data are not available. Therefore, in this study, the value \( \beta = 0 \) was assumed for \( g > 40 \). It is seen in Fig. 1 that taking account of the nonspherical shape has a significant effect on \( \Delta \Phi_g \); along with a wide maximum \( (g = 68, \text{Fig. 1a}) \) typical of the classical theory [1], a number of additional sharp maxima and deep minima emerge. The maxima \( (g_1 = 16, g_2 = 26, g_3 = 32) \) are related to unfilled electron shells and, as a consequence, with increased values of \( q_0 \) and the minima, to unfilled and almost filled shells \( (g_4 = 19, g_5 = 40) \). At lower temperatures (Fig. 1b), the “classical” maximum disappears, and the critical size is defined by the highest peak at \( g = g_1 \). Its emergence is caused by the fact that the threshold of formation of a nucleus in a cluster is almost doubled due to strong deformation, as compared to the spherical model [5, 6] (from 9 to 17 atoms).

The existence of a deep minimum of \( \Delta \Phi_g \) at \( g = g_2 \) means that clusters of this size are stable or metastable. Their concentration may be so high that the flux of clusters departing from the nucleation zone due to diffusion may be comparable with flow in the space of dimensions or even much greater (in the case of spherical clusters, such a situation would be unrealistic). By nucleation zone, we mean the region in the neighborhood of a maximum of supersaturation, which has a nonuniform spatial distribution. Phoretic forces acting on clusters in inhomogeneous fields of temperature and vapor concentration may intensify this effect. The clusters departing from the nucleation zone decay, which reduces the flow of survivable embryos of the liquid phase. In view of this fact, we will write the equations of kinetics of homogeneous nucleation in the form

\[
\frac{d n_g}{dt} = I_{g-1} - I_g - \delta_{g,s} \frac{n_g}{\tau_d},
\]

where \( n_g \) is the concentration of clusters of the size \( g \);

\[
I_g = n_g \nu_g^+ - n_{g+1} \nu_g^- \]

is the flow of clusters in the space of dimensions; \( \nu_g^+ \) and \( \nu_g^- \) are the frequencies of condensation and evaporation of atoms on the surface of clusters containing \( g \) atoms, respectively; \( \delta_{g,s} \) is the Kronecker symbol; and \( \tau_d \) is the characteristic time of cluster diffusion from the nucleation zone. In writing equation (8), it was assumed that the diffusion term could be ignored for all sizes of \( g \neq g_2 \); as usual, only the evaporation and condensation of single atoms were included.

In writing the condensation frequency, which is proportional to the cluster surface area, its nonspherical shape may be ignored:

\[
\nu_g^+ = C n_g r_g^2 (g/\eta_g)^{3/2} (8 \pi k_B T/M)^{1/2},
\]

where \( C \) is the condensation coefficient and \( M \) is the atomic mass. The evaporation frequency is defined by the principle of detailed balance and formula (1):

\[
\nu_g^- = (\bar{n}_g/\bar{n}_{g+1}) \nu_g^+.
\]

Under stationary conditions \( (dn_g/dt = 0) \), it follows from equations (8) that the cluster flux is constant in the space of dimensions both at \( g < g_2 \) \((I_g = J)\) and at \( g \geq g_2 \) \((I_g = J)\). At \( g = g_2 \), the cluster departure from the nucleation zone breaks the continuity of flow: \( J - J = n_{g_2}/\tau_d \). In so doing, the number of clusters \( J \) capable of infinite growth, which are formed in unit volume per unit time (the nucleation rate), is defined by the formula

\[
J = S(1, \infty) + \frac{\bar{n}_g}{\tau_d} S(1, g_2 - 1) S(g_2, \infty).
\]

Here, \( S(i,j) = \sum_j^j (\nu_g^+/\bar{n}_g)^{-1} \). Under conditions of Fig. 1a and at \( \tau_d = \infty \), formula (9) transforms to the classical formula for nucleation rate [2].
Under conditions corresponding to Fig. 1b, only the sizes corresponding to sharp maxima of $\Delta \Phi_g$ at $g = g_1$ and $g_3$ contribute to the sums in formula (9) (the contribution by the maximum at $g_4$ is small, see Section 4), and equation (9) takes the form

$$\frac{1}{J} = \frac{1}{\nu g_1 \bar{n}_{g_1}} \left(1 + \frac{\bar{n}_{g_2}}{\tau_d \nu g_3 \bar{n}_{g_3}}\right). \quad (10)$$

It is seen from (10) that the cluster departure from the nucleation zone may noticeably influence the nucleation rate if $\frac{\bar{n}_{g_1}}{\tau_d \nu g_3 \bar{n}_{g_3}} > 1$. The inequality $\frac{\bar{n}_{g_1}}{\bar{n}_{g_3}} \gg 1$ helps make this condition valid. At $\tau_d = \infty$, equation (10) reduces to

$$J = \frac{C n_1^2 r_c^2 (g_1/\eta)^{2/3}}{(8\pi k_B T/M)^{1/2} (n_1/K_z)^{g_1}}. \quad (11)$$

Formula (11) coincides with the result of [5] (formula (11b)) if it is assumed that $N = g_1/\eta$. Note that the critical size $g_1$ is independent of the parameters of state of vapor, and the nucleation rate is independent of the saturation pressure and value of surface tension. In equation (11), these quantities are replaced by dimer parameters, which characterize the interatomic potential.

The values of critical supersaturation $S_{cr}$, at which $J = 2 \text{ cm}^{-3} \text{s}^{-1}$, were calculated for cesium vapor using formulas (1), (3), (5), (6), and (9). In so doing, it was assumed that $C = 1$, and the quantity $\tau_d$ was defined by Brownian diffusion of clusters from the nucleation zone. The calculation results are shown in Fig. 2. At $T > 490 \text{ K}$, the situation corresponds to Fig. 1a: the size of the critical nucleus (more than 60 atoms) and the values of $S_{cr}$ almost do not differ from those calculated by the classical nucleation theory. At lower temperatures, the maximum of $\Delta \Phi_{16}$ proves to be lower than the “classical” one (Fig. 1b); the critical size decreases by a jump to 16 atoms and is no longer dependent on the parameters of state; in so doing, formula (9) yields higher values of $S_{cr}$ than the classical theory. For comparison, Fig. 2 shows the results of experiment [10] for the case of the maximum ratio of diameter of the experimental setup to its height—in the opinion of the experimenters, these data have a minimum error. It is seen that both the calculated and experimental data lie above the results of the classical theory. Note that the spherical model would yield values of $S_{cr}$, which almost do not differ from the classical ones.

A sharp increase in $S_{cr}$ at $T < 430 \text{ K}$ and subsequent disappearance of nucleation in the experiment [10] is unlikely to be true. At low temperatures, the weak dependence of the measured nucleation rate on the supersaturation estimated disregarding the nucleation is apparently indicative of vapor depletion (decrease of its concentration caused by condensation). In this region, the possibility of systematic error is not rejected by Cha et al. either.
4. STATISTICAL INTERPRETATION OF THE MODEL

Similar to [5], the results obtained above are based on the general assumption that the chemical potential of a cluster is a linear function of the numbers of its surface and inner molecules. In the given case of cesium vapor, the nucleation rate at relatively low temperatures is defined by the number density of 16-atom clusters, all of whose atoms are surface ones. For these clusters, the chemical potential is linearly dependent on the total number of atoms. Statistical interpretation of such dependence may be based on the assumption that, at sufficiently high temperatures, clusters containing 10–20 molecules or less are in states in which molecules form chains (more precisely, virtual chains). By virtual chain we will mean any spatial configuration of molecules in which the nearest neighbors of each molecule, except for the first and last ones, are the preceding and subsequent molecules. As a result of thermal motion, the order of succession of molecules in chains is continuously changing.

A transition to spatial configurations of the type of virtual chains is a consequence of statistical “competition” between compact states with a high binding energy but small statistical weight and states with the minimum number of bonds \((g - 1)\) for \(g\)-molecule cluster but great statistical weight of translational motion. In order to qualitatively analyze the possibility of such transition, consider the simplest realization of a cluster: the system containing 10–20 molecules or less are in states in which molecules form chains (more precisely, virtual chains). By virtual chain we will mean any spatial configuration of molecules in which the nearest neighbors of each molecule, except for the first and last ones, are the preceding and subsequent molecules. As a result of thermal motion, the order of succession of molecules in chains is continuously changing.

In order to qualitatively analyze the possibility of such transition, consider the simplest realization of a cluster: the system containing \(g\) atoms interacting by means of a short-range pair additive potential \(u(r)\) characterized by two length parameters, \(a\) and \(r_0\). Let \(u(r) = +\infty\) at \(r < a - r_0\) and \(u(r) = 0\) at \(r > a + r_0\); \(u(r) = (M\omega_0^2/4)(r - a)^2 + D_0\) on the segment \([a - r_0, a + r_0]\), where \(\omega_0 = (2r_0)/\sqrt{D_0/M}\) is the frequency of dimer oscillation and \(D_0\) is the well depth. For a short-range potential, the ratio \(a/r_0\) is a great parameter.

We will write the partition function of a cluster in two limiting cases: at low and high temperatures. In the former case, the cluster has a crystal-like structure; its rotational and vibrational partition functions are defined by the following relationships (the Einstein model of crystal; the energy is reckoned from the ground state):

\[
Z_r^{(g)} = C_r(g)\left(\frac{a}{\lambda}\right)^3, \tag{12}
\]

\[
Z_v^{(g)} = C_v(g)\left(\frac{k_BT}{\hbar\omega_0}\right)^{3g - 6}, \tag{13}
\]

where \(\lambda = \sqrt{2\pi\hbar^2/Mk_BT}\) is the thermal wavelength, and \(C_r(g)\) and \(C_v(g)\) are numerical factors defined by the crystal structure (for example, \(C_r(3) = 2\pi^2/3\), \(C_v(3) = (4/3)\sqrt{2/3}\)).

In the limiting case of high temperatures, we will use the virtual chain approximation; i.e., we will assume that the potential energy of a light cluster may at any instant be represented in the form

\[
U_c = \sum_{i=1}^{g-1} u(r_{ii+1}), \tag{14}
\]

where \(r_{ii+1} = |r_i - r_{i+1}|\) is the distance between neighboring atoms in a chain. In so doing, all spatial configurations other than virtual chains are assumed to be improbable. Because it is only the preexponential factor in the partition function that depends on the number of chains that form the cluster, we will consider only those states in which atoms form a single chain. Then it is easy to check that the full partition function of a cluster is factorized by means of a linear transformation of the coordinates of atoms whose Jacobian is equal to unity, and the partition function is written in the form

\[
Z^{(g)} = \lambda^{-3g} \int \cdots \int \exp\left(-\frac{U^{(g)}}{k_BT}\right) dr_1 \cdots dr_g
\]

\[
= \frac{V}{\lambda^{3g}} \left(\int \exp\left[-\frac{u(r_{12})}{k_BT}\right] d(r_1 - r_2)\right)^{g-1} \tag{15}
\]

\[
= \frac{V}{\lambda^{3g}} \left[Z_r^{(2)} Z_v^{(2)} \exp\left(-\frac{D}{k_BT}\right)\right]^{g-1}.
\]

Here, the prime designates the integration over a region in which no identical states may occur; \(V\) is the volume. Note that the factor \(g!\) is absent in equation (15), because \(g!\) chains may be constructed of \(g\) atoms.

Partition function (15) is similar to the propagator of a macromolecule [12] with the only difference that the order of succession of atoms in a chain is not fixed (which is a consequence of additivity of the interatomic potential).

Relationships (12), (13), and (15) define the ratio of probabilities of realization of configurations with the minimum \(P_{\text{min}}\) and maximum \(P_{\text{max}}\) numbers of bonds,

\[
\frac{P_{\text{min}}}{P_{\text{max}}} = \left[\frac{Z_r^{(2)} Z_v^{(2)}}{Z_r^{(g)} Z_v^{(g)}}\right]^{g-1} \exp\left(-\frac{\Delta E_g}{k_BT}\right) \tag{16}
\]

\[
= \frac{\pi^{g-1}}{C_r C_v} \left(\frac{a}{r_0}\right)^{2g - 5} \left(\frac{2D_0}{\pi k_BT}\right)^{g - 2.5} \exp\left(-\frac{\Delta E_g}{k_BT}\right),
\]

where \(\Delta E_g = D_g - (g - 1)D_0\) and \(D_g\) is the energy of cluster dissociation at \(T = 0\). It follows from equation (16) that virtual chains dominate if \((2g - 5)\ln(a/r_0) > \Delta E_g/k_BT\). For a short-range potential, \(\Delta E_g\) increases sharply as the first cluster shell is filled [13]; \(\Delta E_g/g \to \infty\) at small \(g\),
5D_g at \( g \to \infty \). Therefore, for a typical case, in which \( a/r_0 \sim 10 \), light clusters are chainlike, and heavy ones are dropletlike; the characteristic transitional size is \( g \sim 10 \). For example, we obtain for a trimer at \( a/r_0 = 6 \), which is characteristic of vibrations in the neighborhood of the bottom of the Lennard-Jones potential, \( P_{\text{min}}/P_{\text{max}} > 1 \) at \( k_bT > 0.43D_o \). This is less than 2/3 of the melting temperature of an argon-like system. For a tetramer, the value of transition temperature practically does not differ from that given above.

5. DISCUSSION

The foregoing results indicate that virtual chainlike configurations dominate in the spatial structure of the lightest clusters at fairly high temperatures. It follows from expression (15) for the partition function of a virtual chain that the chemical potential of a small cluster is a linear function of \( g \):

\[
\mu_g = k_BT\ln(\bar{n}_g \lambda^3) + (A_1 + A_3)g + A_3, \tag{17}
\]

where \( A_1(T), A_2(T), \) and \( A_3(T) \) are functions of temperature. On the other hand, in the limit of a macroscopic droplet (\( g \to \infty \)),

\[
\mu_g = k_BT\ln(\bar{n}_g \lambda^3) + A_2g. \tag{18}
\]

The simplest way of combining dependences (17) and (18) is the linear interpolation

\[
\mu_g = k_BT\ln(\bar{n}_g \lambda^3) + A_1q_0 + A_2g + A_3 \tag{19}
\]

with the additional condition for small clusters \( q_0 = g \), \( q_0 = 0 \) (the absence of inner atoms). Thus, the linear dependence of cluster chemical potential on the numbers of surface and inner atoms, which was postulated in [5] to account for anomalous nucleation rates, may be interpreted as a linear interpolation between the limiting cases of small and large clusters.

One may assume that, if \( \Delta E_g \) increases slowly with \( g \), the virtual chainlike configurations are realized not only for additive short-range potentials. For example, for cesium the increase in \( \Delta E_g \) is moderate: \( D_g/g \to 1.7D_0 \) at \( g \to \infty \), and for a short-range potential, \( D_g/g \to 6D_0 \). This means that virtual chains must emerge in metal clusters as well. This assumption is favored by the fact that the equation of state for cesium vapor [14], derived on the basis of relation (17) (\( \bar{n}_g = n_1(n_1/K_2)^{g^{-1}} \)), is capable of describing experimental data.

In what follows, we will estimate the effect of factors which were disregarded in the calculation of the nucleation rate of cesium vapor. The rate of cluster departure from the nucleation zone is defined by the time \( \tau_g = h^2/2D_g \), where \( D = 0.107\chi(k_BT/m)^{1/2}/n_1r_g^2 \) is the diffusion coefficient of a Brownian particle [15]; \( \chi \) is the ratio of concentrations of cesium vapor and buffer gas; \( m \) is the mass of a molecule of buffer gas (helium); and \( h \) is the thickness of the nucleation zone. This expression yields the upper estimate for \( \tau_g \) and the lower estimate for the flux of departing clusters, because the effect of phoretic forces is ignored. Under real conditions, \( \tau_g \) may be much smaller. For \( \chi \) and \( h \), the values are taken that correspond to experimental conditions [10]: \( 8 \times 10^{-3} \) and 1.5 mm, respectively. In so doing, the ratio \( J/J_1 = 1 + \bar{n}_g, S(g, \infty)/\tau_g \) is of the order of \( 10^1-10^2 \); i.e., the diffusion flux is not small. Its inclusion causes an increase of \( S_g \) by \( 3-6\% \), which appears to be the most significant correction as compared to other unaccounted-for factors (nonisothermality of the process, condensation and evaporation of dimers, etc.).

Consider the sensitivity of the results to the value of the deformation parameter \( \beta \). In 16-atom clusters defining the nucleation rate, the nucleus emerges at \( \beta = -0.30 \). At lower values of \( \beta \), the numbers \( g = q_0 = 16 \), and, in accordance with equations (1) and (9), the nucleation rate is independent of \( \beta \). According to [7], the equilibrium value of \( \beta \) is equal to \( -0.35 \), and in [8] to \( -0.40 \); i.e., the deformation must noticeably exceed the threshold one in absolute magnitude. This fact justifies the use for cesium clusters of the values of \( \beta \) calculated for sodium, as well as neglect of the temperature dependence of this quantity. At \( g < 16 \), the equilibrium values of \( \beta \) differ even more from the threshold ones. The calculation results are also weakly dependent on the value of \( N \); in 16-atom clusters, the nucleus exists only at \( N < 7.2 \).

A high degree of deformation is also characteristic of 32-atom clusters. Their concentration seems to be so small that they are not involved in the nucleation process at all: the transition from the 31-atom to 33-atom cluster and vice versa occurs by condensation (evaporation) of a dimer. In order to take this fact into account, the term with \( g = 32 \) should have been omitted in the sums of formula (9), and \( v_3^+ \) should be multiplied by the factor \( n_1/K_2 \). Under the given conditions, this factor is not too small and is about 0.03; therefore, a sharp peak at \( g = 32 \) (Fig. 1) has almost no effect on the nucleation rate (it is reduced by less than 1%), and it may be ignored. Note that tunneling of a wide maximum at \( g = 16 \) may be ignored in virtue of smallness of the number densities of clusters with \( g \geq 9 \) required for this purpose.

The anomalous nucleation rate in mercury vapor is well described by the spherical model. This is not surprising, because the nonmetallic van der Waals type of bond is characteristic of small mercury clusters, and the factor which breaks the isotropy is absent. In contrast, the type of bond in cesium clusters is metallic for any size including the smallest one. As a result, the electron subsystem acquires nonzero total orbital momentum, which is the reason for nonspherical shape. In the same model, with due regard for nonspherical shape, it proves possible to describe deviations from the classi-
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REFERENCES
